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Inventors: Nobuo KIMURA *et al.*

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For: METALLIC PLATE OR RESIN STRUCTURE HAVING PHOTO-CATALYST-SUPPORTING FILM LAMINATED THERETO

Art Unit: 1754

Examiner: Edward M. Johnson

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Submission of Translations of Priority Documents

Commissioner for Patents
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Sir:

This paper is filed in response to the Office Action of March 10, 2004.

A translation of the priority documents, JP09/322248 and JP/09/322247, together with the Declaration of Mr. Kazuto Murayama, the translator, are submitted herewith.

No fee is believed to be required for this filing; however, if a fee is determined to be necessary, please charge the amount to our Deposit Account No. 22-0261, and notify the undersigned accordingly.

Date: June 10, 2004

Respectfully submitted,

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE		
In re: U.S.Patent Application of ; Nobuo KIMURA et al. Serial No. 09/530,196 Filing Date November 5, 1998 For METALLIC PLATE OR RESIN STRUCTURE HAVING PHOTOCATALYST-SUPPORTING FILM LAMINATED THERETO		Group: 1754 Examiner: Edward M. Johnson Atty Dkt: 31981-160441 U.S.P.T.O. Customer No. **26694**
		May 31, 2004

DECLARATION / TRANSLATION CERITIFICATION

Assistant Commissioner for Patentes
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I, Kazuto Murayama hereby declare that:

I am familiar with the English and Japanese languages and I am a professional translator from Japanese to English.

I am employed by the translation company which bears the name HIROTA $ ASSOCIATES.

I prepared a translation of the documents JP09/322248 and JP09/322247, Reference No. 97YA22 and Reference No. 97YA21, respectively; those translations are attached to this declaration.

To the best of my knowledge and belief, the translations are literal and fairly reflect the contents and meaning of the original documents.

I further declare under penalty of perjury under the laws of the United of States of America that the forgoing is true and correrct.

Executed on May 31, 2004

Kazuto Murayama

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【Type of Document】 Specification

【Title of the Invention】 Metallic Plate having Photocatalyst-Supporting Film Laminated Thereto

【Claims】

【Claim 1】 A metallic plate laminated with a photocatalyst-supporting film characterized in that the metallic plate is obtainable by laminating a photocatalyst-supporting film onto the surface of the metallic plate by heat-pressing and is having photocatalytic activity capable of decomposing triolein at a rate of 5μg/cm²/day or more when irradiating UV rays in UV-A range at a strength of 3 mW/cm² under an atmospheric temperature of 25 ℃ and relative humidity of 70%.

【Claim 2】 The metallic plate laminated with a photocatalyst-supporting film according to Claim 1 characterized in that the photocatalyst-supporting film is made of polymer resin film in which a photocatalyst layer is carried on the film via an adhesive layer.

【Claim 3】 The metallic plate laminated with a photocatalyst-supporting film according to Claim 2 characterized in that the polymer resin film is a film on which 2 or more resin films are laminated.

【Claim 4】 The metallic plate laminated with a photocatalyst-supporting film according to Claim 2 or Claim 3 characterized in that the polymer resin film is made of a resin selected from a group consisting of polycarbonate resins, copolymers of 2 or more of polymethylmetacrylate resins or polyacrylate resins, poly(vinyl chloride) resins and cellophane resins.

【Claim 5】 The metallic plate laminated with a photocatalyst-supporting film according to any of Claims 2 through 4 characterized in that the thickness of the polymer resin film is in a range of from 5 to 200μm.

【Claim 6】 The metallic plate laminated with a photocatalyst-supporting film according to any of Claims 2 through 5 characterized in that the adhesive layer is formed by coating a coating solution for an adhesive layer containing a silane coupler as a hardener.

【Claim 7】 The metallic plate laminated with a photocatalyst-supporting film according to Claim 6 characterized in that a coating solution for an adhesive layer prepared by adding a silane coupler in an amount of 0.1-5% by weight relative to the weight of the coating

solution as a hardener to a coating solution composed of a silicon denaturated resin in an amount of 2-20% by weight which contains either polysiloxane in an amount of 10-50% by weight or colloidal silica in an amount of 5-30% by weight is used for the coating solution for an adhesive layer.

【Claim 8】 The metallic plate laminated with a photocatalyst-supporting film according to Claim 6 characterized in that a coating solution prepared by adding a silane coupler as a hardener in an amount of 0.1-5% by weight relative to the weight of the coating solution into a solution containing either monoalkyltrimethoxysilanes or its hydrolyzed product in an amount of 1-10% by weight and silica sol in an amount of 0.1-5% by weight is used as the coating solution for an adhesive layer.

【Claim 9】 The metallic plate laminated with a photocatalyst-supporting film according to any of Claims 2 through 8 characterized in that the thickness of the adhesive layer is in a range of from 0.5 to 5 μm.

【Claim 10】 The metallic plate laminated with a photocatalyst-supporting film according to any of Claims 2 through 9 characterized in that the photocatalyst layer contains a metal oxide sol in an amount of 1-10% by weight as solid component and titanium dioxide in an amount of 1-10% by weight as solid component.

【Claim 11】 The metallic plate laminated with a photocatalyst-supporting film according to any of Claims 2 through 9 characterized in that the photocatalyst layer contains silica sol in an amount of 1-10% by weight, either of monoalkyltrimethoxysilane or its hydrolyzed product in an amount of 1-10% by weight and titanium dioxide in an amount of 1-10% by weight.

【Claim 12】 The metallic plate laminated with a photocatalyst-supporting film according to Claim 10 or Claim 11 characterized in that the thickness of the photocatalyst layer is in a range of from 0.1 to 5 μm.

【Claim 13】 The metallic plate laminated with a photocatalyst-supporting film according to any of Claims 1 through 12 characterized in that the metallic plate is a metallic plate selected from a group consisting of iron plate, steel plate, aluminium plate and aluminium

alloy plate.

【Claim 14】 The metallic plate laminated with a photocatalyst-supporting film according to any of Claims 1 through 13 characterized in that the metallic plate is any of resin-coated metallic plate, paint-coated metallic plate and enamelled metallic plate, which are coated in either single or multiple layers with one or more resins selected from a group consisting of poly(vinyl chloride) resins, polyethylenetelephthalate resins and polymethylmetacrylate resins.

【Claim 15】 The metallic plate laminated with a photocatalyst-supporting film according to any of Claims 1 through 14 characterized in that the shape of the metallic plate is any of plate-form, tubular and corrugated-form.

【Claim 16】 A method for preparing a metallic plate laminated with a photocatalyst-supporting film characterized in that the laminated metallic plate is prepared firstly by coating a coating solution for an adhesive layer wherein a silane coupler as a hardener is added onto a polymer resin film and then drying it and subsequently coating a coating solution for a photocatalyst layer onto the adhesive layer and then drying it to prepare a photocatalyst-supporting film which carries the photocatalyst layer on the polymer resin film via the adhesive layer, and then laminating the photocatalyst-supporting film onto the surface of the metallic plate by applying heating and pressing.

【Claim 17】 Reflection plates for lighting equipments, outdoor-use signboards and other signs, home-use electric appliances, guardrails and road signs using the metallic plate laminated with a photocatalyst-supporting film according to any of Claims 1 through 15 at least for the part of them.

【0001】

【 Field of Invention 】

The present invention is related to a metallic plate, a metallic plate coated with resin, a painted metallic plate and an enameled metallic plate, which are obtainable by laminating thereto a photocatalyst-supporting film having deodorant, antiflouling, antibacterial, antifungal and other effects by means of heat-pressing, a method for preparing such metallic plates and various products for which such metallic plates are applicable.

【0002】

【 Prior Arts 】

Titanium dioxide, which is n-type semiconductor, has been known as a photocatalyst that activates various chemical reactions with ultraviolet radiation energy, such as chemical reactions resulted in during a process of pasteurization and decomposition of organic substance. On the other hand, various methods to carry a photocatalyst layer onto a glass plate, plastics, tiles, etc. have been proposed (See JP Laid-opened No. Sho 62-66861 and No. Hei 5-309267, EP 633064 and USP 4888101) have been proposed. However, a metallic plate which is laminated with a photocatalyst-supporting film, particularly the one composed of widely-used polycarbonate resin or cloth-reinforced poly(vinyl chloride) resin and capable of carrying a photocatalyst without loosing photocatalytic activity, has not been known. Further, a method to maintain deodorant, antifouling, antibacterial and antifungal effects for a long time by efficiently utilizing photocatalytic activity given by the metallic plate being laminated with such photocatalyst-supporting film has not been reported.

【0003】

In the past, outdoor installed soundproof walls made of polycarbanate resin plates or a resin reinforced with poly(vinyl chloride)-absorbed fibers get stained easily with dust and smoke, normally develop discoloration thereof and disfigure during a few months. Further, such soundproof walls gets mold growth thereon thanks to great amount of plasticizer components contained in poly(vinyl chloride) resin, and a method to coat a fluororesin onto the surface of such soundproof wall as a countermeasure. However, the coating of a fluororesin tends to increase the water repellent property on the surface and the oil affinity, which makes attaching of dust and smoke to the surface of such resin plates more easier. Based on the characteristic of titanium dioxide that appears to show hydrophilic property when it is subjected to ultraviolet rays in the atmosphere, a method to facilitate washing of attached oil components, such as oil mist, with water, particularly by raining, by making the surface of outdoor structure hydrophilic with titanium dioxide (See JP Laid-open No.63-100042 gazette and WO 96/29375). This is to utilize a mechanism

that the structure surface which becomes hydrophilic makes spreading of water on the surface easier, eventually allowing to float oil components from the surface and to fall down therefrom. However, according to the method disclosed in those gazettes, there is practically a constrain in the application for soundproof walls for roads where great amount of stain, such as exhaust of diesel cars, tend to firmly attach to such walls.

【0004】

In WO 97-134 gazette, an example which enables to provide a resin structure having high photocatalytic activity and excellent durability prepared by means of carrying a photocatalyst layer composed of photocatalyst particles complex containing metal oxide gel thereon via an adhesive layer composed of acrylsilicon resin added with polysilixane by either dipping or spraying method is disclosed. However, according to this invention, though it enables to provide a photocatalyst-supporting film of which reverse side is coated with a sticking agent, there is a disadvantage that photocatalytic activity deteriorates when the film is subjected to laminating process by heat-pressing, that coating of a photocatalyst at high speed film formation get problematic due to insufficient hardening of an adhesive layer.

【0005】

A photocatalyst-supporting film prepared by providing a photocatalyst layer composed of a photocatalyst complex containing a metal oxide gel via an adhesive layer composed of an acrylsilicon resin added with polysiloxane onto a polyester film is capable of maintaining high photocatalytic activity and excellent durability, and this film is disclosed in WO 97-134. However, it is generally difficult to laminate the polyester film by means of heat-pressing and such film cannot be used for the purpose according to the present invention.

【0006】

In addition, with the composition of the disclosed coating solution in WO 97-134, there is a disadvantage that the coated film tend to attach to the reverse side thereof due to insufficient drying and hardening of the coated layer during high speed film formation. In particular, a film which can be laminated by heat-pressing has low temperature property as to thermal resistance and thermal deformation

as low as 100℃, it is difficult to carry out high speed formation of a film which is applicable for heat-laminating process by using the coating solution and coating method disclosed in WO 97-134, and photocatalytic activity may disappear depending upon the condition of heat-laminating process given. Whereas, According to the application by dipping or spraying, it is practically not applicable in view of constrains in production facilities, film formation speed and drying speed in case of plate-shaped large metal plates. However, such method has problems in production cost, since it requires long drying process after coating, and particularly in case of a metallic plate longer than one meter, a big size drier and long drying process more than 30 minutes are required, which is the cause to make production speed slow and high cost.

【0007】

For carrying a photocatalyst onto a metallic plate, a coated metallic plate, a resin-coated metallic plate and an enamelled metallic plate for aiming at providing antiflouling, antibacterial and deodorant activity thereto, a method to directly provide a photocatalyst structure which is supporting a photocatalyst layer via an adhesive layer onto a metallic plate or the like can be employed. However, this method requires longer time for drying process after coating than the case of film formation. Namely, in view of heat capacity, at least minute level duration is required for drying when directly forming a film onto a metallic plate, whereas only second level duration is enough for drying when taking such film formation process. Therefore, from production efficiency point of view, taking film formation is more advantageous even taking the time required for laminating film into consideration, if the shape of the metallic plate is flat sheet-like.
This method has other disadvantages such that the metallic plate might be corroded and gets rust during drying process owing to pH condition of an adhesive layer and a photocatalyst layer and that coating of homogeneous film onto a metallic plate by dipping or spraying to cause the thickness of the film irregular particularly in case that the size of the metallic plate is larger than one meter, thereby giving limitation in the type and size of applicable metallic plates.

【0008】

【Problems to be solved by the invention】

It is an object of the present invention to provide metallic plates, resin-coated metallic plates, paint-coated metallic plates or enamelled metallic plates, which are laminated with a photocatalyst-supporting film having excellent deodorant, antifouling, antibacterial, antifungal effects, etc.

【0009】

【Means for Solving Problem】

It is an object of the present invention to provide a process to efficiently laminate a transparent photocatalyst-supporting film at high speed by heating and a photocatalyst-supporting film of which photocatalytic activity is not inferiorly influenced by heat-laminating process of the photocatalyst-supporting film, which enables to carry on a photocatalyst onto surface of a film which is suitable to give lamination thereon at high speed with good production efficiency. And, the objective is found to be achieved by providing an invention to laminate a polymer resin film having photocatalytic activity, which can decompose triolein at a rate of 5μm/cm²/day or more under irradiation of UV rays in UV-A region at a rate of 3 mW/ cm² and at an atmospheric temperature of 25℃ and relative humidity of 70%, onto the surface of a metallic plate by applying heating and pressing.

【0010】

Namely, the present invention is related to a metallic plate laminated with a photocatalyst-supporting film being obtainable by laminating a photocatalyst-supporting film composed of a polymer resin film, whereto a photocatalyst layer is carried on via an adhesive layer, by applying heating and pressing onto the surface of the metal plate and having photocatalytic activity capable of decomposing triolein at a rate of 5 μg/cm²/day or more by irradiating ultraviolet rays in UV-A range at a strength of 3 mW/cm² under condition of atmospheric temperature of 25 ℃ and relative humidity of 70%.

【0011】

The present invention is also related to a metallic plate being laminated with the said photocatalyst-supporting film, characterized in that said polymer resin film is one obtained by laminating at least two types of resin films, that the polymer resin is one selected from a

group consisting of polycarbonate resins, copolymerization resins of at least two types of polymethylmetacrylate resins and/or polyacrylate resins, poly(vinyl chloride) resins and cellophane resins, that the thickness of the polymer resin film is in a range of from 5 to 200 μm, that the adhesive layer is formed by coating a coating solution containing a silane coupler as a hardener, that the coating solution for an adhesive layer is prepared by adding a silane coupler in an amount of 0.1-5% by weight based on the weight of the coating solution as a hardener into a coating solution containing a denaturated silicon resin in an amount of 2-20% by weight based on the weight of the later coating solution, and the denaturated silicon resin contains either 10-50% by weight of polysiloxane or 5-30% by weight of colloidal silica, that the coating solution for an adhesive layer is prepared by adding a silane coupler in an amount of 1-5% by weight based on the weight of the coating solution as a hardener into a coating solution which contains either of monoalkyltrimethoxysilane or its decomposed-product, polysiloxane, in an amount of 1-10% by weight and silica sol in an amount of 0.1-5% by weight based on the later coating solution, that the thickness of the adhesive layer is in a range of from 0.5 to 5 μm, that the photocatalyst-supporting layer contains a metal oxide sol in an amount of 1-10% by weight as a solid component and titanium dioxide sol in an amount of 1-10% by weight as a solid component, that the photocatalyst-supporting layer contains silica sol in an amount of 1-10% by weight, either of monoalkyltrimethoxysilane or its hydrolyzed product in an amount of 1-10% by weight and titanium dioxide sol in an amount of 1-10% by weight, that the thickness of the photocatalyst-supporting layer is in a range of from 0.1 to 5μm, that the metallic plate is one selected from a group consisting of an iron plate, a stainless steel plate, an aluminium plate and an aluminium alloy plate, that the metallic plate is any of a resin-coated metallic plate, a coated metallic plate and an enamelled metallic plate, which are coated either in a single layer or in multiple layers with one or more than two resins selected from a group consisting of poly(vinyl chloride) resins, polyethylenetelephathalate resins and polymethylmetacrylate resins, and that the shape of the metallic plate is sheet-like, tubular or corrugated.

【0012】

Further, the present invention is related to a process for preparing a metallic plate laminated with a photocatalyst-supporting film characterized in that the process is constituted of the first process to coat and then to dry a coating solution for an adhesive layer added with a silane coupler as a hardener onto a polymer resin film, the second process to coat and then to dry a coating solution for a photocatalyst layer onto the adhesive layer to prepare the photocatalyst-supporting film which carries a photocatalyst layer onto the polymer resin film via the adhesive layer and the third process to laminate the photocatalyst-supporting film onto the surface of the metallic plate by applying heating and pressing process.

【0013】

Again, the present invention is related to reflection plates for lighting fixtures, outdoor signboards, home-use electric appliances, guardrails and road signs which are using the metallic plate laminated with the photocatalyst-supporting film described above at least as a part.

【0014】

【Mode for Carrying Out the Invention】

The metallic plate laminated with a photocatalyst-supporting film is prepared firstly by coating a coating solution for an adhesive layer containing a silane coupler as a hardener onto a film, for example a polymer resin film, then drying the coating solution, and subsequently coating a coating solution for a photocatalyst layer, then drying the coating solution for a photocatalyst layer to prepare a photocatalyst layer on the polymer resin film via an adhesive layer, and then laminating by heating and pressing the photocatalyst-supporting film onto the surface of the metallic plate. The cross section illustration for the inventive metallic plate laminated with the photocatalyst-supporting film is shown in Fig. 1.

【0015】

For examples of the material used for the polymer resin film specified in the present invention, polycarbonate resins, copolymer resins made of at least two polymethylmetacrylate resins and/or polyacrylate resins, nylon resins, polyamide resins, polyimide resins,

polyacrylonitrile resins, polyurethane resins, poly(vinyl chloride) resins, cellophane resins, polyvinylalcohol resins, vinyl acetate-ethylene copolymer resins and ethylene-vinyl alcohol copolymer resins are given. However, it is preferable to use such materials that have both tensile strength and elastic modulus enough to resist to a given tension caused by a film-forming apparatus in order to avoid causing spreads and wrinkles of the film at coating the solution and forming the photocatalyst layer and the adhesive layer and to obtain a homogeneous and uniform photocatalyst-supporting film.

【0016】

Among the resins as exemplified above, it is particularly preferable to use a film composed of any of polycarbonate resins, copolymers resins made of at least two polymethylmetacrylate resins and/or polyacrylate resins, poly(vinyl chloride) resins and cellophane resins, and the photocatalyst-supporting film using any of these resins has excellent properties in all of photocatalytic activity, durability, film-forming performance, laminating performance, lower cost, etc. Further, the use of a film prepared by laminating two or more of these films described above can greatly improve important properties for a photocatalyst-supporting film, particularly weather-resistance, heat-resistance, moisture permeability, etc. Therefore, it is possible to design and change the property of the photocatalyst-supporting films depending upon the condition where the film is to be used, which is more advantageous for industrial scale production thereof.

【0017】

The thickness of the polymer resin film to be used in the present invention is preferably in a range of from 5 to 200 μm, and the formation of both adhesive layer and photocatalyst layer becomes difficult when the thickness is less than 5 μm, whereas the laminating work becomes difficult and requires higher cost when the thickness is more than 200 μm.

【0018】

The photocatalyst-supporting polymer resin film of the present invention to be used for the lamination onto a metallic plate has a structure wherein an adhesive layer is provided in between the photocatalyst layer and the film, as shown in Fig. 1. The adhesive

layer is prepared by coating and then drying a coating solution for an adhesive layer onto the film, which has a role to firmly adhere a photocatalyst layer onto the film and prevents the deterioration of the activity of the photocatalyst caused by a plasticizer component spreading from the film or the polymer resin laminated with the film and degradation of the film due to photocatalytic effect, and the adhesive layer itself has a characteristic being resistant to the photocatalytic effect.

【0019】

For the coating solution for an adhesive layer, the one which contains a silane coupler as a hardener is preferably used. Incorporation of the silane coupler into the coating solution for an adhesive layer enables to accelerate the hardening of the adhesive layer to form a film, which allows to wind the film without causing sticking of the adhesive layer to the reverse side of the film, thereby enabling the formation of the film at high speed. Further, The incorporation of the silane coupler can prevent the deterioration of photocatalytic activity of the photocatalyst-supporting film laminated onto the surface of a metallic plate by means of heating and pressing and allows to maintain the photocatalytic activity owned by the photocatalyst-supporting film before subjecting it to laminating process.

【0020】

For an example of the coating solution for an adhesive layer, the one prepared by adding a silane coupler as a hardener in an amount of 0.1-5% by weight based on the weight of the coating solution containing at a concentration of 2-20% by weight either a silicon denaturated resin containing 10-50% by weight of polysiloxane or a silicon denaturated resin containing 5-30% by weight of colloidal silica, into the coating solution is given.

【0021】

In case of using a silicon denaturated resin, such as acrylsilicon resins and epoxysilicon resins, which contains polysiloxane at a concentration of less than 10% by weight, or a silicon denaturated resin which contains colloidal silica at a concentration of less than 5% by weight, for the coating solution for an adhesive layer, adhesivity of the photocatalyst layer at the time of light irradiation gets

insufficient, and the adhesive layer decomposes due to photocatalytic effect of outdoor strong ultraviolet rays, whereby easy exfoliation of the adhesive layer is caused. Whereas, in case of using a silicon denaturated resin which contains more than 50% by weight of polysiloxane or more than 30% by weight of colloidal silica, adhesion between the adhesive layer and a carrier structure gets insufficient, the adhesive layer gets porous, or adhesion between carrier film and the adhesive layer gets insufficient, thereby causing easy exfoliation of photocatalyst layer from the film.

【0022】

Further, for an example of the coating solution for an adhesive layer, the one prepared by adding a silane coupler as a hardener in an amount of 0.1-5% by weight based on the weight of the coating solution into a mixture of silica sol and either of monoalkyltrimethoxysilane or the hydrolyzed product, polysiloxane. For examples of the monoalkyltrimethoxysilane, monomethyltrimethoxysilane and monoethyltrimethoxysilane are preferably given. For the silica gel, it is preferable to use the one having the finest primary particle size, and it is particularly preferable to use the one having a primary particle size less than 20 nm for obtaining a transparent film. To the coating solution, it is preferable to incorporate 0.1-5% by weight of silica gel and either of monoalkyltrimethoxysilane or its hydrolyzed product, polysiloxane, at a concentration of 1-10% by weight for obtaining better adhesive property and catalytic activity. The rate for the amount of silica gel and either of monoalkyltrimethoxysilane or the hydrogenated product is preferably in a range of from 80/20 to 40/60, and addition of an acid catalyst, such as mineral acid, may be useful to accelerate hardening.

【0023】

The amount of the silane coupler as a hardener to be added is preferably in a range of from 0.1 to 5% by weight based on the weight of the coating solution for an adhesive layer, even though the coating solution is composed of polysiloxane-silicon denaturated resin, colloidal silica-silicon denaturated resin or monoalkyltrimethoxysilane-silica sol. In case that the added-amount of the silane coupler is less than 0.1% by weight, the coated-layer sticks to the reverse side of the

film when winding the coated-film following to drying, thereby making subsequent coating of the photocatalyst layer difficult. Whereas, in case that the added-amount of the silane coupler is more than 5% by weight, hardening of the coating solution goes too fast or the coating solution gels during the formation of the film. When the silane coupler in an amount of 0.1-5% by weight based on the weight of the coating solution is applied, photocatalytic activity does not deteriorate, even though the photocatalyst-supporting film is laminated onto the surface of a metallic plate by means of heating and pressing, and the photocatalytic activity can be maintained to the same level as one given before laminating process.

【0024】

For the silane coupler, compounds represented by general formulas, $RSi(X)_3$ and $(R)_2Si(X)_2$, wherein R represents an organic functional group and X represents chlorine or alkoxy, can be used, and wherein R represents methyl, ethyl, vinyl, γ-glycidoxypropyl, γ-metacryloxypropyl, γ-(2-aminoethyl)aminopropyl, γ-chloropropyl, γ-mercaptopropyl, γ-aminopropyl, γ-acryloxypropyl or the like and X represents chlorine and C_{1-5} alkoxy, such as methoxy, ethoxy and β-methoxyethoxy.

【0025】

Whereas, for a purpose to prevent deterioration of the adhesive layer due to influence of the photocatalytic activity and to improve the durability, a photostabilizing agent and/or an ultraviolet absorbent or the like may be incorporated into the adhesive layer. As usable photostabilizing agents, it is preferable to use hindered amine compounds, however, any other photostabilizing agents can be used as well. Whereas, triazole compounds can be used as the ultraviolet absorbent. The amount of the ultraviolet absorbent to be added into the coating solution is in a range of from 0.005% by weight to 10% by weight based on the weight of the coating solution, and more preferably from 0.01% by weight to 5% by weight. The incorporation of a photostabilizing agent and/or a UV absorbent into the adhesive layer enables to improve the weather resistance of a polymer resin film carrying a photocatalyst, which gives an advantage when it is used at outdoor. In addition, addition of a surface active agent in an amount

of 0.00001-0.1% by weight into the coating solution for an adhesive layer enables to get excellent metallic plates laminated with the photocatalyst-supporting film.

【0026】

For coating an adhesive layer onto a film, a method to coat a coating solution for an adhesive layer by means of gravure, microgravure, comma coating, roll coating, reverse roll coating, bar coating, kiss coating and flow coating, then to dry the coating solution can be given. Appropriate temperature during the drying process can be different depending on a coating method, a solvent used, a type of a resin used for a film and thickness of a film, however, it is preferably at 150 ℃ or less.

【0027】

The thickness of the adhesive layer is preferably $0.5\mu m$ or more. When the thickness is less than $0.5\ \mu m$, an effect to firmly adhere the photocatalyst layer onto a film gets insufficient and the photocatalyst layer may exfoliate from the film after long time use. Although it is not a substantial problem to make the adhesive layer thick, however, drying during the formation of the adhesive layer gets insufficient, thereby causing the layer irregular and raising the cost for forming the adhesive layer.

【0028】

The photocatalyst-supporting polymer resin film according to the present invention to be used for lamination onto a metal plate has a structure that an adhesive layer is provided on a photocatalyst layer, as shown in Fig.1. The photocatalyst layer can be formed by coating a coating solution for photocatalyst layer which, for example, contains 1-10% by weight of metal oxide sol as solid component and 1-10% by weight of titanium dioxide sol as solid component and then drying the solution. The metal oxide sol contained in the coating solution for a photocatalyst layer works not only to fix the titanium dioxide sol and firmly adhere it to an adhesive layer but also to enhance photocatalytic activity owing to its absorption property based on the porous structure of the gel obtained by drying the metal oxide sol. Ratio of the metal oxide sol and the titanium dioxide sol in the coating solution for a photocatalyst layer is preferably in a range of from 25/75 to 95/5.

Adhesion to the adhesive layer gets insufficient when the ratio of the metal oxide sol is less than 25%, whereas photocatalytic activity gets insufficient when the ratio is more than 95%. Further, when the specific surface area of the gel that is obtained by drying the metal oxide sol is 100 m²/g or more, the adhesivity get more firm as well as improvement in the photocatalytic activity. For an example of the metal in the metal oxide sol, silicon, aluminium, titanium, zirconium, magnesium, niobium, tantalum and tungsten are preferably given, and mixtures of these metal oxide sol and complex oxide sols prepared by coprecipitation method, etc. can be used as well.

【0029】

When mixing a metal oxide sol with titanium dioxide sol, it is preferable to mix it in sol state or in a state being at before preparing into the sol. As a method to prepare the sol, a method to hydrolyze the metal salt, a method to decompose it under neutral condition, a method to subject it to ion exchange, a method to hydrolyze the metal alkoxide, etc. can be given, however, any methods which allow to obtain the sol wherein titanium dioxide sol is homogeneously distributed can be employed. However, it is more preferable to use a sol which contains less impurities since such impurities in greater amount in the sol may give unfavorable effects on adhesivity of a photocatalyst and its photocatalytic activity. In particular, when organic substance in an amount more than 5% by weight relative to the dry weight of the sol is contained in the sol, photocatalytic activity may be decreased. Particularly, it is more preferable to use zirconium oxide sol or aluminium oxide sol to prepare a photocatalyst layer, since it may facilitate to get through tape exfoliation tests after having either 15 min. resistance test to boiling water or dipping test for 168 hours into 5% sodium carbonate solution.

【0030】

Whereas, it is particularly preferable to use a coating solution for a photocatalyst layer which is composed of a mixture of silica sol in an amount of 1-10% by weight, either monoalkyltrimethoxysilane or its hydrolyzed-product in an amount of 1-10% by weight and titanium dioxide sol in an amount of 1-10% by weight for coating onto an adhesive layer to obtain a photocatalyst layer. For the monoalkyltrimethoxysila

ne, it is more preferable to use methyltrimethoxysilane and methyltriethoxysilane. The ratio to mix silica sol with either monoalkyltrimethoxysilane or its hydrolyzed-product, it is preferable to select a rate by weight of from 100/0 to 60/40, whereas as a rate by weight of titanium dioxide sol to a silane compound, it is preferable to use a ratio of from 5/95 to 75/25. In case that the ratio for the silane compound is more than 95, photocatalytic activity may be decreased, while adhesivity to an adhesive layer may be decreased when the ratio is lower than 25.

【0031】

For the photocatalyst in a photocatalyst layer, TiO_2 ZnO, $SrTiO_3$ CdS, GaP, InP, GaAs, $BaTiO_3$, K_2NbO_3, Fe_2O_3, Ta_2O_5, WO_3, SnO_2, Bi_2O_3, NiO, Cu_2O, SiC, SiO_2, MoS_2, InPb, RuO_2, CeO_2, etc. can be given. Further, any photocatalysts as exemplified above whereto a metal, such as Pt, Rh, RuO_2, Nb, Cu, Sn and NiO, and their oxide compounds, is incorporated can be also used. The content of a photocatalyst in a photocatalyst layer is preferably lower than 75% by weight in view of adhesivity, though photocatalytic activity increase along with increase of the content. In order to further improve antibacterial and antifungal activities, it is also useful to incorporate a metal or a metallic compound in an amount of 0.05-5% by weight relative to the weight of titanium dioxide photocatalyst in a photocatalyst layer. When the incorporated-amount of such metal compound is less than 0.05% by weight, the improving effect on antibacterial and antifungal activity is poor, while discoloration of a photocatalyst layer may be caused when the incorporated-amount of a metal compound is more than 5% by weight, which may give constrain to use such a photocatalyst layer depending upon the color or design of a resin structure laminated with a film.

【0032】

For the formation of a photocatalyst layer on an adhesive layer, a suspension wherein a photocatalyst is dispersed in either a metal oxide sol or a metal hydroxide sol can be used according to the coating method as described above in the formation of an adhesive layer. Alternatively, a photocatalyst can be dispersed in a precursor solution of such metal oxide or metal hydroxide, then to prepare sol or gel of

such metal oxide or metal hydroxide by subjecting them to hydrolysis or decomposition under neutral condition at coating. When such sol is used, a deflocculant, such as an acid and an alkali, may be added for stabilizing the sol suspension. By adding a surface active agent or a silane coupler in an amount of 5% by weight relative to the weight of a photocatalyst into the sol suspension to improve adhesivity and handling efficiency. However, the addition of a silane coupler into a photocatalyst layer cannot prevent decrease in photocatalytic activity at a process to laminate a photocatalyst-carrying film onto the surface of a metallic plate or a resin structure by heating and pressing and facilitate to maintain the photocatalytic activity owned by a photocatalyst-supporting film before the laminating process. Temperature at forming a photocatalyst layer is preferably 150℃ or lower, though appropriate temperature may differ depending upon coating method, a material used for a film or resin type of an adhesive layer.

【0033】

The photocatalytic activity increases along with the increase of thickness of a photocatalyst layer, however, in a range more than 5 μm, no more increase of photocatalytic activity is recognized. The photocatalyst layer having thickness less than 5 μm shows high photocatalytic activity, still has light permeability and makes a photocatalyst layer less distinguished, whereas the photocatalyst layer in less than 0.1 μm thick has high light permeability, but it allows ultraviolet rays to be utilized by a photocatalyst passing therethrough, whereby unable to obtain high photocatalytic activity. High photocatalytic activity can be obtained by making the thickness of a photocatalyst layer to a range of from 0.1 to 5 μm and using a photocatalyst crystals having a particle size of 40 nm or less and either a metal oxide gel or a metal hydroxide gel having a specific surface area of 100m²/g or more. In this case, it is also favorable to use such photocatalyst layer in view of picture because it does not defile the appearance of metallic plates, resin-coated metallic plates, coated metallic plates or enamelled metallic plates to which a base film is laminated.

【0034】

For the metal plate to be laminated with a photocatalyst-supporting

film by heating and pressing, any kind of metallic plates being typically-used, such as an iron plate, a stainless plate, an alloyed stainless plate, an aluminium plate, an aluminium alloy plate, etc. can be used. For the metallic plate, in addition to simply using a metallic plate as it is, a metallic plate coated in single layer or multiple layers with one or more resins selected from a group consisting of poly(vinyl chloride) resins, polyethylenetelephthalate resins and polymethylmetacrylate resins, a metallic plate coated with paints, an enamelled metallic plate, etc. are also preferably used. As to the shape of the metallic plate, any shape which may suit for laminating a photocatalyst-supporting film thereon, such as sheet-like, tubular and corrugated sheet-like, can be selected.

【0035】

As a method to laminate the photocatalyst-supporting film onto various types of metallic plates, a method to laminate the film onto a metallic plate, a paint-coated metallic plate, a resin-coated metallic plate and an enamelled metallic plate, while heating and pressing the film by using a heated roller or the like, a method to laminate a photocatalyst-supporting polymer resin film by heating and pressing, which utilizes heat being applied during manufacturing of resin structures, onto a paint-coated metallic plate, a resin-coated metallic plate or an enamelled metallic plate, are preferably used because these methods allow industrially efficient manufacturing. For the lamination of the photocatalyst-supporting film by heating and pressing onto a metallic plate, it is preferable to employ a laminating method by short time heating normally at a temperature of from 60 to 200 ℃ though it depend on the material of the resin used for the base film, a laminating method by heating and pressing which utilizes heat arising at heating and drying process for coating a resin or paints onto a metallic plate structure, a laminating method by heating and pressing which utilizes heat arising at molding a metallic plate structure, and the like can be preferably employed.

【0036】

Further, in case of a metallic plate of which structure surface is not processed to chemical or coating treatment, it is possible to further improve the film adherence and resistance of the heat-laminated